NASA-CR-205564

056867

PROJECT CLOSING REPORT

"PLASMA-SPRAYED REFRACTORY OXIDE COATINGS ON SILICON-BASE CERAMICS"

(NCC-3-285)
(Project Period: 3/01/93-11/15/96)

Submitted to:

NASA-Lewis Research Center
Cleveland, OH 44135

by:

Prof. Surendra Tewari,
Department of Chemical Engineering Deprtment,
Cleveland State University,
Cleveland, OH 44115

Sept 18, 1997

PLASMA-SPRAYED REFRACTORY OXIDE COATINGS ON SILICON-BASE CERAMICS

INTRODUCTION

Silicon-base ceramics are promising candidate materials for high temperature structural applications such as heat exchangers, gas turbines and advanced internal combustion engines. Composites based on these materials are leading candidates for combustor materials for HSCT gas turbine engines. These materials possess a combination of excellent physical and mechanical properties at high temperatures, for example, high strength, high toughness, high thermal shock resistance, high thermal conductivity, light weight and excellent oxidation resistance.

However, environmental durability can be significantly reduced in certain conditions such as when molten salts, H2 or water vapor are present. The oxidation resistance of silicon-base materials is provided by SiO2 protective layer. Molten salt reacts with SiO2 and forms a mixture of SiO2 and liquid silicate at temperatures above 800C. Oxygen diffuses more easily through the chemically altered layer, resulting in a catastrophic degradation of the substrate. SiC and Si3N4 are not stable in pure H2 and decompose to silicon and gaseous species such as CH4, SiH, SiH4, N2, and NH3. Water vapor is known to slightly increase the oxidation rate of SiC and Si3N4.

Refractory oxides such as alumina, yitria-stabilized zirconia, ytria and mullite (3Al2O3.2SiO2) possess excellent environmental durability in harsh conditions mentioned above. Therefore, refractory oxide coatings on silicon-base ceramics can substantially improve the environmental durability of these materials by acting as a chemical reaction barrier. These oxide coatings can also serve as a thermal barrier.

The purpose of this research program has been to develop refractory oxide chemical/thermal barrier coatings on silicon-base ceramics to provide extended temperature range and lifetime to these materials in harsh environments.

PROPOSED RESEARCH AND TECHNICAL BACKGROUND

Research at Solar Turbines, Inc. and Oak Ridge National Lab showed that refractory oxide

coatings on SiC tend to crack on thermal cycling. It is not surprising that alumina or ytria-stabilized zirconia coatings crack on thermal cycling considering the high thermal expansion mismatch between these oxides (»9x10-6/oC for alumina and »11x10-6/oC for ytria-stabilized zirconia) and silicon-base ceramics (»3-5x10-6/oC), which is likely to produce a high thermal stress. However, thermal expansion coefficient (CTE) of mullite (»5.4x10-6/oC) is fairly close to that of silicon-base ceramics that CTE mismatch may not be the major factor for the observed cracking.

When molten mullite is rapidly quenched, crystallization is suppressed and metastable amorphous mullite is formed. Crystallization of amorphous mullite occurs at »1000C which is accompanied by a shrinkage of volume, resulting in a high residual stress. In a previous study by Lee et.al., phase transformation of amorphous mullite during thermal cycling was identified as the key factor for the observed poor thermal shock resistance of plasma-sprayed mullite. Solid solution range of mullite is dependent on the processing route and is very difficult to control. Plasma spray of mullite tends to precipitate second phase Al2O3 and SiO2 which may also cause a high residual stress and thus contribute to the cracking. During previous research at NASA it was seen that deposition of metastable amorphous mullite was feasible, and that this process could yield significant improvement of thermal shock resistance.

Since oxide ceramics with less amount of SiO2 possess better environmental resistance in hydrogen or molten salts, it is desirable to apply alumina, ytria-stabilized zirconia or ytria overlayer coatings on mullite base coating for further enhancement of the environmental durability of silicon-base ceramics. CTE mismatch between mullite and these oxides are so substantial that a high thermal stress is likely to develop at the interface on thermal cycling. However, CTE of materials can be tailored by mixing two or more materials with different CTEs. Therefore, CTE mismatch between mullite base coating and alumina, ytria- stabilized zirconia or ytria overlayer coatings can be minimized by applying compositionally gradient coatings of mullite and these oxides.

In the following section we will list the major accomplishments during this research project.

KEY ACCOMPLISHMENTS

A. Development of Environmental/Thermal Barrier Coatings for Si-Based Ceramics: Silicon-based ceramics are the leading candidate materials for high temperature structural applications. However, an environmental protection scheme is necessary to realize the full potential of these materials. Key environmental issues include molten salt corrosion and evaporation of silica in reducing gases or water vapor, leading to a rapid recession of material. This task was aimed at developing protective refractory oxide coating systems for Si-based ceramics to provide protection from these severe environments.

A. 1. Characterization of Long-Term Durability of Mullite Coating for SiC Ceramics: A new fully-crystalline mullite coating was developed in our laboratory. New mullite(5-10 mil)-coated sintered SiC and SiC/SiC composites were tested for long-term environmental durability and chemical compatibility by cycling the sample between room temperature and 1200/1300°C with 1 or 2 hr cycle. No macroscopic cracking or spallation of coating occurred after over 500 cycles. After 600 cycles at 1200°C, mullite showed excellent thermal shock resistance and chemical compatibility (only limited oxidation at the interface). After 250 cycles at 1300°C, mullite still showed excellent thermal shock resistance; however, substantial oxidation of SiC occurred, leading to the formation of a large number of pores at the coating/SiC interface. Continued formation of pores may cause the delamination of coating in long term exposures at 1300°C.

Thermally-cycled mullite-coated SiC (600 1hr cycles at 1200°C) was tested for molten salt corrosion. It exhibited excellent resistance to molten salt corrosion in a burner rig (Jet A fuel, 2ppm Na, 4 Atm, 50 hr). This confirmed the potential of mullite as a barrier coating against molten salt corrosion.

Mullite-coated SiC/SiC composite exposed to a rich burn gas in a high pressure burner rig at 1260°C revealed a selective evaporation of silica from the surface. This will lead to a rapid recession of mullite coating. Therefore, an overlay coating such as yttria-stabilized zirconia (YSZ) is necessary to protect the recession of SiC ceramic from reducing gases or water vapor.

A. 2. *Development and Characterization of Mullite/YSZ Dual Layer Coatings*: YSZ is more stable than mullite in reducing gases or water vapor because it has much lower vapor pressure than silica and it is not known to form a hydroxide. Mullite is used as a bond coat because of its

excellent thermal shock resistance and chemical compatibility. YSZ was applied onto new mullite bond coat by conventional plasma spraying. Mullite(5 mil)/YSZ(5 mil)-coated SiC and SiC/SiC composites were cycled between room temperature and 1200/1300°C with 2hr cycle. No macroscopic cracking or spallation of coating occurred after over 350 cycles. After 250 cycles at 1200°C, mullite/YSZ coating showed excellent thermal shock resistance and chemical compatibility (similar to the mullite coating/SiC system). Only limited reaction was observed at the mullite/YSZ interface after 250 cycles at 1300°C. However, substantial cracking occurred around the mullite/YSZ interface after 250 cycles at 1300°C. This is likely due to the large CTE mismatch between mullite and YSZ (5.6×10^{-6} °C^{-1} for mullite *vs* 10-12 x 10^{-6} °C^{-1} for YSZ) and the resultant thermal stress. Phase transformation of YSZ from tetragonal (as-sprayed) to cubic and monoclinic (1300°C in long exposure) may be another contributor to the cracking. YSZ stays as tetragonal at 1200°C even in long exposure. Cracking becomes more severe with a thicker YSZ---5 mil mullite/15 mil YSZ coating showed a massive cracking only after 20 hr at 1260°C in a high pressure burner rig.

SiC or SiC/SiC composites exhibit paralinear oxidation when exposed to reducing gases or water vapor due to the evaporation of silica by SiO(g) or $Si(OH)_4$, respectively. Similar behavior is expected for mullite-coated SiC. When mullite(5 mil)/YSZ(5 mil) coating was applied on SiC/SiC composites, the weight loss portion from the paralinear oxidation was eliminated in 50% H_2O-50% O_2 at 1300°C. This demonstrated that mullite/YSZ coating is a promising system to protect SiC from evaporation in reducing gases or water vapor.

A. 3. Development of Mullite and Mullite-Based Coatings for Si_3N_4 Ceramics: Because of industries' current need to protect Si_3N_4 ceramics from molten salt environments, mullite coating technique developed for SiC ceramics has been applied to Si_3N_4 ceramics. Two major technical barriers have been identified. First, there is a significant CTE mismatch between Mullite and Si_3N_4 ceramics (5.6×10^{-6} °C^{-1} for mullite *vs* 3-4 x 10^{-6} °C^{-1} for Si_3N_4 ceramics). Second, it is very difficult to roughen the surface of Si_3N_4 ceramics, which is essential to achieve a good mechanical bonding at the coating/substrate interface.

B. Characterization of Cyclic Oxidation Behavior of Superalloys and Superalloy-Matrix Composites for EPM Nozzle Backstructure

Cyclic oxidation study of MA956 and sapphire/MA956 composites has been completed. Distinctively different cracking behavior was observed in monolithic MA956 and composite. Oxidation lifetime was projected based on the oxidation kinetics data. Stress analysis of the system using finite element analysis explained the different cracking behavior.

C. Characterization of Thermal Protection Systems for EPM Nozzle Thermal Blankets

Environmental durability and thermal properties of candidate thermal protection systems for ELM nozzle thermal blankets have been tested. Test includes thermal aging at high temperatures in furnace and subsequent exposure to burner rig.

PUBLICATIONS

1. K,N. Lee, R.A. Miller, and N.S. Jacobson, "Development of Thermal Shock Resistant Mullite Coatings on Silicon Carbide," Ceramic Transactions Vol 38, 565-575 (1994).
2. K.N. Lee and R.A. Miller, "Long-Term Durability of Mullite-Coated Silicon-Based Ceramics," Ceramic Engineering & Science Proceedings Vol.A, 547-554, July-August, 1994.
3. K.N. Lee, N.S. Jacobson, and R.A. Miller, "Refractory Oxide Coatings on SiC Ceramics," *MRS Bulletin,* **14**[10] 35-38 (1994).
4. K.N. Lee, N.S. Jacobson, and R.A. Miller, "Refractory Oxide Coatings on SiC Ceramics," NASA TM 106677, 1994.
5. K.N. Lee and W.L. Worrell, "High-Temperature Oxidation Behavior of Iridium-Based Alumina-Forming Ternary Intermetallics," *Oxid. Met.* Vol 41, 37-63 (1994).
6. K.N. Lee and R.A. Miller, "Refractory Oxide Coatings on Silicon-Based Ceramics," HITEMP Review 1994, 62/1-62/9 (1994).
7. K.N. Lee, V.K. Arya, G.R. Halford, and C.A. Barrett, "Kinetics of Cyclic Oxidation and Cracking and Finite Element Analysis of MA956 and Sapphire/MA956 Composite System (PART I-EXPERIMENTAL)," HITEMP Review 1994, 51/1-51/10 (1994).
8. K.N. Lee, V.K. Arya, G.R. Halford, and C.A. Barrett, "Kinetics of Cyclic Oxidation and Cracking and Finite Element Analysis of MA956 and Sapphire/MA956 Composite System (PART II-ANALYTICAL)," HITEMP Review 1994, 52/1-52/12 (1994).
9. K.N. Lee, R.A. Miller, and N.S. Jacobson, "New Generation of Plasma-Sprayed Mullite Coatings on SiC," (J. Am. Ceram. Soc.)
10. K.N. Lee and N.S. Jacobson, "Chemical Stability of the Fiber Coating/Matrix Interface in Silicon-Based Ceramic Matrix Composites," (J. Am. Ceram. Soc.)
11. K.N. Lee, V.K. Arya, G.R. Halford, and C.A. Barrett, "Kinetics of Cyclic Oxidation and Cracking and Finite Element Analysis of MA956 and Sapphire/MA956 Composite System,".
12. K.N. Lee and R.A. Miller, "Durability of Mullite Coatings On SiC And SiC/SiC Composites under Thermal Cycling Between Room Temperature and 1200-1400^{o}C," (J. of Mat. Sci.)
13. K.N. Lee, R.A. Miller, N. S. Jacobson, and E.J. Opila, "Environmental Durability of Mullite Coating/SiC and Mullite-YSZ Coating/SiC Systems," (1995 Cocoa Beach Meeting)

14. N.S. Jacobson, K.N. Lee, and T. Yoshio, "Corrosion of Mullite by Molten Salts."

PRESENTATIONS

1. 18th Annual Conference of Composites and Advanced Ceramics, January 9-12, 1994, Cocoa Beach, FL.
2. Aeromat'94 Conference, June 6-9, 1994, Anaheim, CA.
3. Hitemp Review 1994, October 24-26, 1994, Westalke, OH.

PATENT DISCLOSURES PROPOSED

1. CVD SiC/Plasma-Sprayed Mullite Dual Layer Coating Systems for Silicon-Nitride Ceramics.
2. Mullite/Glass Ceramic/Mullite/Yttria-Stabilized Zirconia Multilayer Coating System for Silicon-Based Ceramics.

CLEVELAND STATE UNIVERSITY
GRANT EQUIPMENT INVENTORY

UPDATE _____ INTERIM _____ FINAL X

GRANT NO: NWIR-26 (NCC-3-285) SUPPL. NO. (If Applicable) _____ ORS NO. NWIR-26

GRANT BEGINNING DATE: 3/01/93 GRANT EXPIRES ON: 11/15/96

PROJECT DIRECTOR/PRINCIPAL INVESTIGATOR: SURENDRA TEWARI (PRINT NAME) S. Tewari (SIGNATURE) 9/11/96 (DATE)

GRANT TITLE: Plasma sprayed Refractory Oxide Coatings on Silicon based Ceramics

GRANTEE-ACQUIRED EQUIPMENT: EQUIPMENT WHOSE ACQUISITION COST IS $1,000 OR GREATER THAT WAS PURCHASED OR FABRICATED WITH GRANT FUNDS BY A GRANTEE

DESCRIPTION	MODEL #	CSU REQ. NO.	ACQ. DATE	EQUIP COST	*COND. CODE	TAG NO.	LOCATION
Flow Controller		194701	1/11/95	1277.00	4		
486 DX-2-66MHZ Computer		194705	1/31/95	3178.30	4		

THE PRINCIPAL INVESTIGATOR WISHES TO RETAIN POSSESSION OF THIS EQUIPMENT UPON EXPIRATION OF THE GRANT: YES X NO _____

(USE ADDITIONAL SHEETS IF NECESSARY)

EQUIPMENT CONDITION CODES:
4 = GOOD
5 = FAIR
6 = POOR
7 = REPAIRS REQ'D (< 15% OF ACQ COST)
8 = REPAIRS REQ'D (16-40% OF ACQ COST)
9 = REPAIRS REQ'D (41-65% OF ACQ COST)
X = SALVAGE (> 65% OF ACQ COST)
S = SCRAP (VALUE IS MATERIAL CONTENT ONLY)

NASA GRANTEE SUBCONTRACTOR
NEW TECHNOLOGY SUMMARY REPORT

NASA requires each research grantee, research contractor, and research subcontractor to report new technology to the NASA Technology Utilization Office. The required reports and corresponding schedules are as follows:

Title of Report	Form Number	Timetable
New Technology Disclosure	NASA 666A	The grantee subcontractor discloses *each* discovery of new technology individually, at the time of its discovery.
NASA Grantee Subcontractor New Technology Summary Report (checkmarked "Interim")	NASA C-3044	For multi-year grant subcontracts, the subcontractor summarizes the previous year's disclosures on an annual basis. The first Interim New Technology Summary Report is due exactly 12 months from the effective date of the grant.
NASA Grantee Subcontractor New Technology Summary Report (checkmarked "Final")	NASA C-3044	The grantee subcontractor submits a cumulative summary of all disclosed discoveries. The Final New Technology Summary Report is submitted immediately following the grant's technical period of performance.

Subcontractor Name and Address: S. N. TEWARI, CHEMICAL ENGINEERING DEPT
CLEVELAND STATE UNIVERSITY
CLEVELAND (OH) 44115

Report Submitted by: S. N. TEWARI

Telephone Number: (216) 523-7342

NASA Grant Title: PLASMA-SPRAYED REFRACTORY OXIDE COATINGS ON SILICON BASE CERAMICS

NASA Grant Number: NCC 3-255

NASA Grant Monitor: Leslie A. Greenbauer-Seng

Subcontractor Completion Date: 11/15/96

Today's Date: 4/12/97

New technology may be either patentable or non-patentable.
Large business subcontractors must disclose PATENTABLE and NON-PATENTABLE items (i.e., any invention or discovery conceived or first reduced to practice during the performance of the or subcontract) as they are discovered.

Although small business subcontractors are not required to disclose non-patentable new technology, all disclosed NON-PATENTABLE and PATENTABLE new technology items are automatically evaluated for publication as NASA *Tech Briefs*. If an item is selected for publication as a NASA *Tech Brief*, a $150 check payable to the subcontractor innovator is awarded.

PLEASE COMPLETE THE REVERSE SIDE OF THIS FORM AND MAIL TO THE FOLLOWING ADDRESS:

NASA Lewis Research Center
Attn: Kathy Kerrigan
Commercial Technology Office; Mail Stop 7-3
Cleveland, Ohio 44135

RESEARCH
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JUL 1 1994
CLEVELAND STATE UNIVERSITY

Joseph G. Stumpf
Director, Physical Sciences Group

101 North Wilmot Road, Suite 600
Tucson, Arizona 85711-3335
(602) 748-4400
Fax (602) 748-0025

June 28, 1994

Mr. Charles Urbancic
Interim Director
Office of Research Services
Cleveland State University
1983 East 24th Street
Cleveland, OH 44115

Re: RCT Disclosure No. 198A-B323-94
Plasma-Sprayed Mullite/Glass Ceramic Dual Layer Coating
for Silicon-Based Ceramics; K. N. Lee & R. A. Miller

RCT Disclosure No. 198A-B324-94
Plasma-Sprayed Mullite/Yttria-Stabilized Dual Layer Coating
for Silicon-Based Ceramics; K. N. Lee & R. A. Miller

Dear Mr. Urbancic:

This will confirm our recent telephone conversation.

We note that one of the co-inventors of the referenced disclosures is a US government employee. This being the case, the US government has ownership rights to these inventions. These rights could have a negative impact on Research Corporation Technologies' (RCT) ability to license these technologies.

As a result, we are declining to proceed further with an evaluation.

If the US government is willing to relinquish its rights or to assign its rights to Cleveland State University, RCT would be pleased to proceed with a technical and commercial evaluation.

Thank you for your interest in RCT. Please contact me if you have any questions.

Very truly yours,

Joseph G. Stumpf

c: B. Weinberg

JGS:dm

National Aeronautics and
Space Administration

Lewis Research Center
Cleveland, Ohio
44135

NASA

July 7, 1994

Reply to Attn of

Attn: Mr. Charls Urbancic
Research Services
Cleveland State University
Cleveland, OH 44115

Dear Mr. Urbancic:

Enclosed is my invention disclosure entitled, "Mullite/Glass Ceramic/Mullite/Yttria-Stabilized Zirconia Multilayer Coating System for Silicon-Based Ceramics."

I strongly recommend that Cleveland State University assigns the right of the invention to NASA-Lewis Research Center because NASA-Lewis has a great interest in this invention and also has the facility and expertise to fully develop it.

Considering the great technological implication of this invention, immediate processing of the patent application will be very much appreciated.

Sincerely,

Kang N. Lee

RECEIVED
OFFICE OF RESEARCH SERVICES
JUL - 8 1994
CLEVELAND STATE UNIVERSITY

RESEARCH CORPORATION TECHNOLOGIES
Invention Disclosure Form

I. Description

Please provide a title for your invention and a brief description. Inventions include new processes, products, apparatus, compositions of matter, living organisms—OR improvements to (or new uses for) things that already exist. Use additional sheets and attach descriptive materials to expand answers to questions. (Sketches, drawings, photos, reports and manuscripts will be helpful.)

A. Invention Title Mullite/Glass Ceramic/Mullite/Yttria-Stabilized Zirconia Multilayer Coating System for Silicon-Based Ceramics

B. Description A New multilayer coating system of mullite/glass ceramic/mullite/yttria-stabilized zirconia on silicon-based ceramics by plasma spraying, which provides excellent thermal as well as environmental protection in severe environments containing molten salts, water vapor and/or reducing atmosphere.

C. What are the immediate and/or future applications of the invention?

Potential immediate applications include thermal/chemical barrier coatings for combustors for advanced gas turbine engines and protective coatings for heat exchangers and advanced inter combustion engines.

D. Why is the invention better—more advantageous—than present technology? What are its novel and unusual features? What problems does it solve?

Provide a complete protection of silicon-based ceramics in molten salts, water vapor, and/or reducing atmospheres. Combine the benefits of mullite, glass ceramic and zirconia coatings.

E. Is work on the invention continuing? Are there limitations to be overcome or other tasks to be done prior to practical application? Are there any test data?

No limitations to be overcome prior to practical application.

Test data available to confirm its durability and adherence.

Work will continue to further optimize the process.

F. Have products, apparatus or compositions, etc. actually been made and tested?

The coating system was processed and tested (Figs 1a and 1b).

II. Publications, Public Use and Sale

Note: valid patent protection depends on accurate answers to the following items.

A. Has invention been disclosed in an abstract, paper, talk, news story or a thesis?

Type of disclosure _____ Disclosure Date _____

(Please enclose a copy)

Mullite/Glass Ceramic/Mullite/Yttria-Stabilized Zirconia Multilayer Coating for Silicon Carbide

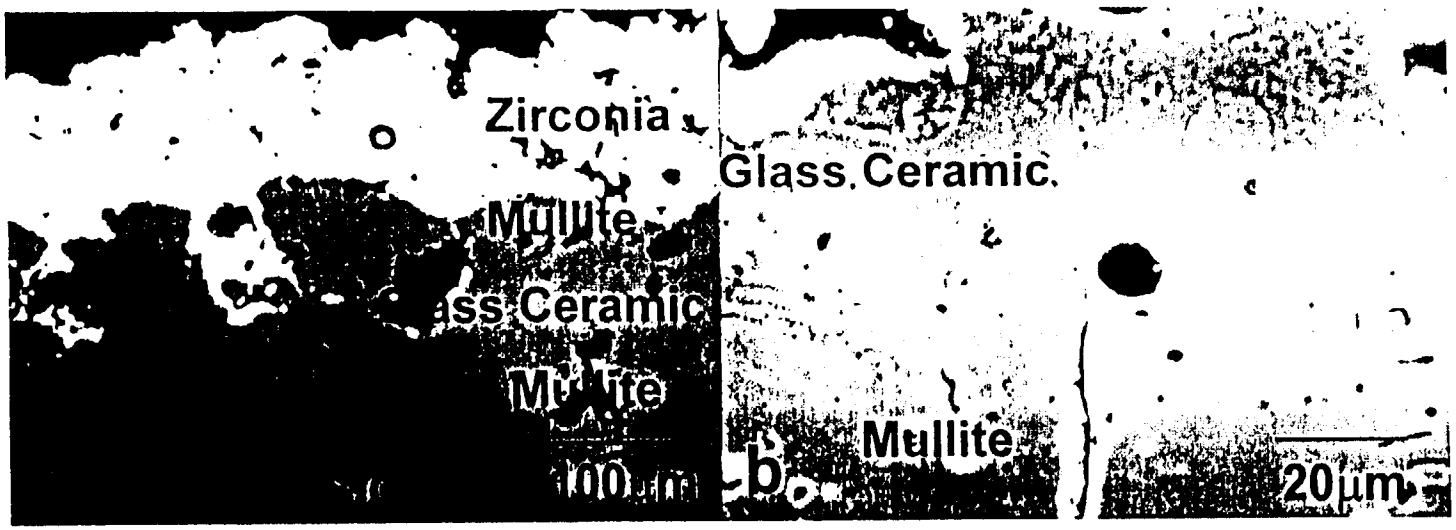

Fig.1. Mullite acts as a bond coat and as a chemical barrier at the glass ceramic/ zirconia interface, zirconia provides thermal and chemical protection from the environments, and glass ceramic stops the crack propagation.

NASA GRANTEE SUBCONTRACTOR
NEW TECHNOLOGY REPORT

NASA requires each research grantee, research contractor and research subcontractor to report new technology to the NASA Technology Utilization Office. The required reports and corresponding schedules for research grantee subcontractors are as follows:

Title of Report	Form Number	Timetable
Individual Disclosure	NASA 666A	The grantee subcontractor discloses each discovery of new technology individually, at the time of its discovery.
Interim Report	LeRC-GSNTR	For multi-year grant subcontracts, the subcontractor summarizes the previous year's disclosures on an annual basis. The first Interim New Technology (NT) Report is due exactly 12 months from the effective date of the subcontract.
Final Report	LeRC-GSNTR	The grantee subcontractor submits a cumulative summary of all disclosed discoveries. This Final NT Report is submitted immediately following the subcontract's technical period of performance.

Subcontractor Name and Address: Cleveland State University
1960 E. 24th St., Cleveland, OH 44115

Report Submitted by: Kang N. Lee
Telephone Number: (216) 433-5634

NASA Grant Title: _____

NASA Grant Number: NCC3-285

NASA Grant Monitor: _____

Subcontract Completion Date: ___/___/___

Today's Date: 7/6/1994

New technology may be either reportable items or subject inventions.

A reportable item is any invention or discovery, whether or not patentable, that was conceived or first actually reduced to practice during the performance of the contract or subcontract. Large business contractors and subcontractors must disclose reportable items as they are discovered and submit a noncumulative list of these new technology items on an annual basis [ref: Interim NT Report] and a cumulative list at the completion of the contract (or subcontract) period [ref: Final NT Report].

A subject invention is any invention or discovery, which is or may be patentable, that was conceived or first actually reduced to practice during the performance of the contract or subcontract, Small business contractors and subcontractors must, at a minimum, disclose subject inventions as they are discovered and submit a cumulative list of these new technology items on an annual basis [ref: Interim NT Report] and at the completion of the contract (or subcontract) period [ref: Final NT Report].

Grantees, small business contractors and subcontractor are only required to disclose and report patentable items (subject inventions). We request, however, that small business contractors and subcontractors disclose both patentable and nonpatentable (reportable) items, both of which are automatically evaluated for publication as NASA tech briefs and considered for NASA *Tech Brief* awards.

PLEASE COMPLETE THE REVERSE SIDE OF THIS FORM AND MAIL TO THE FOLLOWING ADDRESS:

NASA LEWIS RESEARCH CENTER
ATTN: KAREN GRASSE
TECHNOLOGY UTILIZATION OFFICE; MAIL STOP 7-3
CLEVELAND, OHIO 44135

I General Information

1. Type of Report: (X) Interim ( ) Final

2. Size of Business: ( ) Small ( ) Large (X) Nonprofit Organization

3. Have any nonpatentable new technology items resulted from work performed under this subcontract during this reporting period?
( ) yes ( ) no

4. Have any patentable new technology items resulted from work performed under this subcontract during this reporting period?
(X) yes ( ) no

5. Are new technology items (nonpatentable or patentable) being disclosed with this report?
(X) yes ( ) no

II New Technology Items

Please provide the title(s) of all new and previously disclosed new technology items conceived or first actually reduced to practice under this subcontract. If this is an interim report, previously disclosed items need not be mentioned.

	Title	Internal Docket Number	Patent Appl. Filed	Patentable Item	Nonpatentable Item
1.	Mullite/Glass Ceramic/Mullite/Yttria-Stabilized Zirconia Multilayer Coating System for Silicon-Based Ceramics		( )	( )	( )
2.			( )	( )	( )
3.			( )	( )	( )
4.			( )	( )	( )

III Second and Third Tier Subcontractors

Please complete the following section listing all research subcontractors participating to date. Include each subcontractor's name, address, contact person, and telephone number. If this is an interim report, previously noted subcontractors need not be mentioned.

Use of the forms identified on the reverse side of this page is optional; however, an alternate must at a minimum contain the information required by these forms.

NASA New Technology Report

Form Approved
O.M.B. No. 2700-0009

NT CONTROL NO. *(Official use only.)*

INSTRUCTIONS

This form may be used when reporting inventions, discoveries, improvements or innovations to NASA. Use of this report form is optional; provided, however, that whatever report format is used contain the essential information requested herein.

In completing each section, use whatever detail deemed appropriate for a "full and complete disclosure," as required by the New Technology or Property Rights in Inventions clause. For further guidance as to what constitutes a satisfactory report, please refer to NHB 2170.3, Documentation Guidelines for New Technology Reporting.

Available additional documentation which provides a full, detailed description should be attached, as well as any additional explanatory sheets where necessary.

1. TITLE

Mullite/Glass Ceramic/Mullite/Yttria-Stabilized Zirconia Multilayer Coating System for Silicon-Based Ceramics

2. INNOVATOR(S) *(Name and Social Security No.)* *

Kang N. Lee* [redacted]
Robert A. Miller** [redacted]

3. EMPLOYER *(Organization and division)*

* Dept. of Chem. Eng., CSU
** Materials Division, NASA-Lewis

4. ADDRESS *(Place of Performance)*

*,**: NASA-Lewis, 21000 Brook Park Rd.
Cleveland, OH 44135

SECTION I — DESCRIPTION OF THE PROBLEM THAT MOTIVATED THE TECHNOLOGY DEVELOPMENT *(Enter A.—General Description of Problem Objective; B.—Key or Unique Problem Characteristics; C.—Past History/Prior Techniques; D.—Limitations of Prior Techniques)*

A/B. General Description of Problem Objective/Characteristics

Silicon-based ceramics are leading candidate materials for high temperature structural applications such as heat exchangers, gas turbine engines and advanced internal combustion engines. They have excellent oxidation resistance in clean oxidizing environments due to the formation of protective silica scale (SiO_2). However, durability in high temperature environments containing molten salts, high level of water vapor, and/or a reducing atmosphere can limit their applications. Molten salts react with silica to form liquid silicates which no longer are protective. High levels of water vapor and a reducing atmosphere lead to the evaporation of silica scale via $Si(OH)_4(g)$ and $SiO(g)$, respectively. One approach to overcome these potential environmental limitations is to apply barrier coatings which are environmentally stable in these severe environments. These coatings can serve as thermal barrier coatings as well. This document discloses a concept of and a process for a new multilayer coating system of mullite/glass ceramic/mullite/yttria-stabilized zirconia on silicon-based ceramics by plasma spraying. The new coating system provides silicon-based ceramics with excellent environmental resistance in molten salts, water vapor, and/or reducing atmosphere.

C. Prior Art

Previously, we developed a new plasma-spraying process to apply a fully-crystalline mullite coating on silicon-based ceramics (U.S. patent application #08/031,444). This new fully-crystalline mullite coating exhibited dramatically improved adherence and thermal shock resistance compared to conventionally plasma-sprayed mullite coatings. The new mullite coating provides some protection against molten salt corrosion, especially in acidic salts. We also disclosed inventions of mullite/glass ceramic (12-20-93) and mullite/zirconia (2-8-94) dual layer coatings for silicon-based ceramics. The glass ceramic in the mullite/glass ceramic dual layer coating stops the propagation of through-thickness cracks in mullite, preventing the penetration of molten salts. Zirconia in the mullite/zirconia dual layer coating provides protection against vaporization in high water vapor and reducing atmosphere because it has very low volatility in those environments. The zirconia layer also deflects some through-thickness cracks originating from the mullite layer.

D. Limitations of Prior Art

The prior art does not provide complete protection in environments containing molten salts, high water vapor, and/or reducing atmosphere. Mullite coatings develop through-thickness cracks on repeated cycling. Molten salts can penetrate through the cracks and attack the silicon-based substrate in long term exposures. Mullite also has a fairly high silica activity of about 0.4. Therefore the vaporization of silica in water vapor or reducing atmospheres is still significant enough to limit its usefulness for long term applications. The glass ceramic outer layer in the mullite/glass ceramic dual layer coating has too high of a silica activity to prevent the silica evaporation in high water vapor and reducing atmosphere. The zirconia layer in the mullite/zirconia dual layer coating does not resolve the issue of the through-thickness cracks in the mullite layer, which provides a path for molten salt penetration.

* Supplying this information is voluntary, in accordance with Public Law 93-579 (Privacy Act of 1974). However, it is required for eligibility in the establishment of Space Act monetary awards.

SECTION II – TECHNICALLY COMPLETE AND EASILY UNDERSTANDABLE DESCRIPTION OF NEW TECHNOLOGY THAT WAS DEVELOPED TO SOLVE THE PROBLEM OR MEET THE OBJECTIVE *(Enter as appropriate A.–Specific description of item; B.–State of development; C.–Operation as a unit; D.–Functional operation; E.–Supportive theory; F.–Engineering specifications; G.–Peripheral equipment; H.–Drawings, graphs, etc.; I.–Parts or ingredients lists; and J.–Maintenance, reliability, safety factors)*

Identification of Steps

Since mullite coatings do not provide protection against vaporization in high water vapor and reducing atmospheres, refractory oxides with low silica activity or refractory oxides containing no silica are needed in those environments. Yttria-stabilized zirconia has a much lower vapor pressure than silica or mullite, and is not known to form any hydroxide in water vapor. In addition, yttria-stabilized zirconia has lower thermal conductivity than mullite, making it a more effective thermal barrier coating. However, yttria-stabilized zirconia sprayed directly onto silicon-based ceramics debonds on thermal cycling, presumably due to chemical incompatilibity between zirconia and the silica scale which eventually forms on silicon-based ceramics. The detailed nature of the chemical incompatibility is not known yet, although sintering of zirconia by silica and reaction between yttria and silica have been suggested. Therefore, a chemically compatible intermediate layer such as mullite is needed. We have found that a mullite/yttria-stabilized zirconia dual layer coating exhibits excellent thermal shock resistance and chemical compatibility.

Another issue with mullite coatings is the penetration of salt via through-thickness cracks in long term exposures. Yttria-stabilized zirconia overlay coating on mullite does not resolve this issue. We have discovered that glass ceramic overlay coatings on mullite are very effective in stopping the propagation of through-thickness cracks in mullite layer. Like mullite, however, the glass ceramic does not provide protection against vaporization in high water vapor and reducing atmosphere.

Therefore, the combination of glass ceramic and yttria-stabilized zirconia overlay coatings can potentially resolve all the environmental durability issues mentioned above. In this coating concept, the mullite layer provides strong bonding and chemical compatibility, the glass ceramic layer provides crack arrest, and the yttria-stabilized zirconia provides protection against vaporization. When the glass ceramic has a relatively high silica activity, such as cordierite used in this study, another mullite layer is needed between the glass ceramic and the yttria-stabilized zirconia to prevent chemical reaction between the two layers. Combination of all these concepts results in mullite/glass ceramic/mullite/yttria-stabilized zirconia multilayer coatings. The second mullite layer is not necessary if the glass ceramic is chemically compatible with the yttria-stabilized zirconia.

Mullite, glass ceramic, and yttria-stabilized zirconia powders purchased from commercial vendors were plasma-sprayed onto SiC[1] (2.54cm x 0.45cm x 0.2cm) and SiC/SiC composite[2] (2.54cm x 1cm x 0.3cm). Mullite and glass ceramic were sprayed with our new technique (U.S. patent application #08/031,444 and our invention disclosure of mullite/glass ceramic dual layer coating filed on 12-20-93) to obtain fully-crystalline phase. The principle of the new technique is heating of the substrate before and during the spraying process to maintain the substrate temperature above the crystallization temperature of mullite and glass ceramic (about 1000°C). It is very critical to maintain a uniform substrate temperature because local cold spots below the crystallization temperature or local hot spots can cause the cracking of substrate. Yttria-stabilized zirconia was sprayed with conventional techniques. Powder particle size was between 100 and 200 mesh; plasma gun power was 35-45kw; plasma arc gas was Ar-40% He; and powder carrier gas was argon with flow rates between 2 and 6 SLPM (standard liter per minute). SiC coupons were etched in molten sodium carbonate at 860-900°C for 8-10 hours to produce a surface suitable for good adherence (roughness Ra = 150-250 microinch). SiC/SiC composite coupons were used as received, for they already have appropriate surface roughness.

Coated specimens were cycled between 1300°C and room temperature with two-hour cycle to test the adherence, crack resistance, and chemical compatibility. For each cycle, the coated coupon was inserted into a preheated furnace (1300°C) in air, held in the furnace for two hours and then air-quenched to room temperature. After fifty cycles, metallographic examination revealed that the entire coating was still well bonded without any evidence of chemical reaction between each layer, and glass ceramic layer stopped the propagation of cracks (Figs.1a and 1b).

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[1]Hexoloy™, Carborundum, Niagara Falls, NY.

[2]Dupont, Newark, DE.

SECTION II *(Con.)*

The above results clearly demonstrate that the mullite/glass ceramic/mullite/yttria-stabilized zirconia multilayer coating system can effectively serve as an excellent environmental/thermal barrier coating for silicon-based ceramics in severe environments containing molten salt, water vapor, and/or reducing atmosphere.

Alternate Embodiments

The substrate may be any other silicon-based ceramic/metal such as Si_3N_4 or $MoSi_2$, composites based on SiC, Si_3N_4 or $MoSi_2$, or any other ceramics, metals, or metal alloys. Additional intermediate layers such as microcomposites of mullite/yttria-stabilized zirconia or a compositionally gradient coating is envisioned to reduce the CTE mismatch between each layer. Spray parameters other than those described in this disclosure may be used.

SECTION III – UNIQUE OR NOVEL FEATURES OF THE TECHNOLOGY AND THE RESULTS (OR BENEFITS) OF ITS APPLICATION *(Enter as appropriate A.–Novel or unique features; B.–Development or conceptual problems; C.–Operating characteristics, test data; D.–Analysis of capabilities; E.–Source of error; and F.–Advantages/shortcomings)*

Advantage Over Prior Arts

Prior arts have drawbacks in the following areas: Mullite coating does not provide protection against vaporization in high water vapor and reducing atmosphere, and through-thickness cracks in mullite coating causes penetration by molten salts; Mullite/glass ceramic dual layer coating does not provide protection against vaporization in high water vapor and reducing atmosphere; Mullite/yttria-stabilized zirconia dual layer coating does not resolve the issue of through-thickness cracks. In comparison, however, the new Mullite/glass ceramic/mullite/yttria-stabilized zirconia multilayer coating system provides complete protection in severe environments containing molten salts, high water vapor, and/or reducing atmosphere.

Unique Features of the Technology

The concept of multilayer mullite/glass ceramic/mullite/yttria-stabilized zirconia coating to combine the merits of each layer: strong bonding and chemical compatibility from mullite, crack arrest from glass ceramic, and resistance to vaporization in water vapor and reducing atmosphere from yttria-stabilized zirconia.

Benefits of Application

Substantially extend lifetime of silicon-based ceramics in high temperature structural applications by providing excellent thermal as well as environmental protection in severe environments containing molten salts, water vapor, and/or reducing atmosphere.

SECTION III *(Con.)*

SECTION IV — ADDITIONAL DOCUMENTATION *(Include or list below any pertinent documentation which aids in the understanding or application of the new technology. IF NOT TOO BULKY OR DIFFICULT TO REPRODUCE, INCLUDE COPIES WITH THIS REPORT. For those references or additional documentation available but NOT included in this report (due to their being nonessential to a basic understanding of the new technology and which may be costly to reproduce or handle) complete item A, below)*

A. AVAILABLE DOCUMENTS *(Check and complete)*								
		1. PAPERS, ARTICLES	X	4. ASSEMBLY/MFG. DRAWINGS	X	7. TEST DATA		
		2. CONTRACTOR REPORTS		5. PARTS OR INGRED LIST		8. ASSEMBLY/MFG. PROCED.		
	X	3. ENGINEERING SPECS.		6. OPERATING MANUALS		9. COMPUTER TAPES/CARDS		
	10. OTHER *(Specify)* Notebook of Kang N. Lee and George Leissler (plasma Technician)							

B. INDICATE THE DATES OR THE APPROXIMATE TIME PERIOD DURING WHICH THIS TECHNOLOGY WAS DEVELOPED *(i.e. conceived, constructed, tested, etc.)*

Conceived: 12-9-93
Completion of first model: 4-5-94
First successful operational test: 5-16-94

C. LIST THE FIRST PUBLICATION OR PUBLIC DISCLOSURE OF THE NEW TECHNOLOGY, AND DATES

D. LIST THE DATES AND ANY PARTICULARLY PERTINENT PAGE NUMBERS OF OTHER PUBLICATIONS WHICH ARE AVAILABLE BUT NOT ATTACHED

E. DEGREE OF TECHNOLOGICAL SIGNIFICIANCE *(Check in your best judgment the statement which best expresses the degree of technological significance of this technology)*

☐ 1. MODIFICATION TO EXISTING TECHNOLOGY ☐ 2. SUBSTANTIAL ADVANCE IN THE ART ☒ 3. MAJOR BREAKTHROUGH

COMMENTS

SIGNATURE(S) OF INNOVATOR(S)

Kang N. Lee
Robert A. Miller

Kang N. Lee
Robert A. Miller

DATE 7-6-94

U.S. Government Printing Office: 1987—726-368/61109

Mullite/Glass Ceramic/Mullite/Yttria-Stabilized Zirconia Multilayer Coating for Silicon Carbide

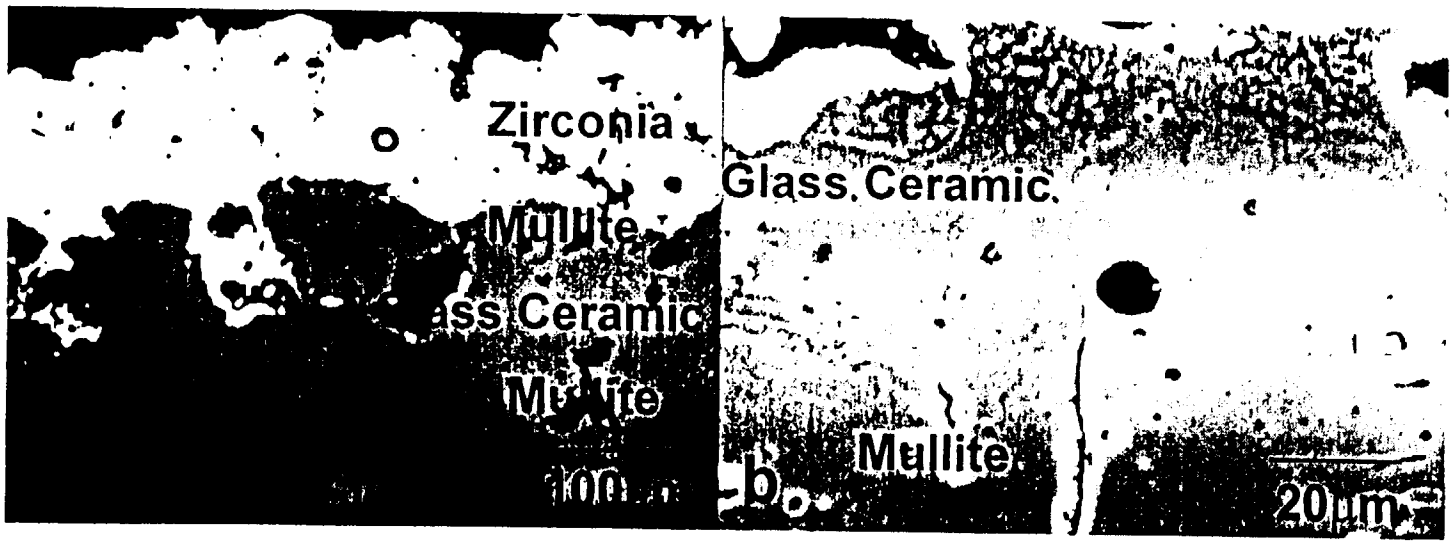

Fig.1. Mullite acts as a bond coat and as a chemical barrier at the glass ceramic/ zirconia interface, zirconia provides thermal and chemical protection from the environments, and glass ceramic stops the crack propagation.

RESEARCH CORPORATION TECHNOLOGIES
Invention Disclosure Form

I. Description

Please provide a title for your invention and a brief description. Inventions include new processes, products, apparatus, compositions of matter, living organisms—OR improvements to (or new uses for) things that already exist. Use additional sheets and attach descriptive materials to expand answers to questions. (Sketches, drawings, photos, reports and manuscripts will be helpful.)

A. Invention Title CVD SiC/Plasma-Sprayed Mullite Dual Layer Coating System for Silicon Nitride Ceramics

B. Description A new multilayer coating system of CVD SiC/mullite on silicon nitride ceramics, which will provide thermal as well as environmental protection in severe environments containing molten salts, water vapor, and/or reducing gases.

C. What are the immediate and/or future applications of the invention?

Potential applications include thermal/environmental barrier coatings for advanced gas turbine engines, advanced internal combustion engines, or heat exchangers.

D. Why is the invention better—more advantageous—than present technology? What are its novel and unusual features? What problems does it solve?

CVD SiC bond coat provides substantially improved bonding of mullite coating compared to the mullite coating alone on silicon nitride ceramics. It also eliminates the extensive roughening process on silicon nitiride ceramics prior to the mullite application.

E. Is work on the invention continuing? Are there limitations to be overcome or other tasks to be done prior to practical application? Are there any test data?

No limitations to be overcome prior to the practical applications

Test data available to confirm its suprior adherence and resistance to thermal cycling

Work will continue to further optimize the process

Have products, apparatus or compositions, etc. actually been made and tested?

The coating system was processed and tested (Fig. 1)

II. Publications, Public Use and Sale

Note: valid patent protection depends on accurate answers to the following items.

Has invention been disclosed in an abstract, paper, talk, news story or a thesis?

Type of disclosure _____ Disclosure Date _____

(Please enclose a copy)

II. (Publications, Public Use and Sale—Continued)

B. Is a publication or other disclosure planned in the next six months?

Type of disclosure _____ Date _____
(Enclose drafts, abstracts, preprints)

C. Has there been any public use or sale of products embodying the invention?

Describe, giving dates _____

D. Are you aware of related developments by others? If "yes," please give citations. Copies of any relevant patents or publications would be appreciated.

No

III. Sponsorship

If the research that led to the invention was sponsored, please fill in the details and attach a copy of the contract or agreement if possible.

A. Government agency NASA-Lewis Research Center contract/grant no. NCC-3-285

B. Name of industry, university, foundation or other sponsor:

C. Has the invention been disclosed to industry representatives? If "yes," please provide details, including the names of companies and their representatives.

No

IV. For Our Records

A. Names and titles of inventors (please print; sign where indicated)

1. Kang N. Lee* Signature Kang Lee Date 3/22/95
2. Robert A. Miller** Signature Robert A. Miller Date 3/22/95
3. Lisa C. Veitch *** Signature Lisa C. Veitch Date 3/22/95

B. Contact for more data Kang N. Lee Tel. (216) 433-5634

C. Mailing address for inventor(s) * 1835 Coe's Post Run, Westlake, OH 44145
** 9224 Highland Dr. Brecksville, OH 44141
*** 18 Stony Brook Ln, Wakeman, OH 44889

D. Name and title of institutional representative (please sign where indicated)

_____ Signature _____ Date _____

Department _____ Tel. (____)

Mailing address _____

RESEARCH CORPORATION TECHNOLOGIES
6840 East Broadway Boulevard
Tucson, Arizona 85710-2815

Telephone 602/296-6400

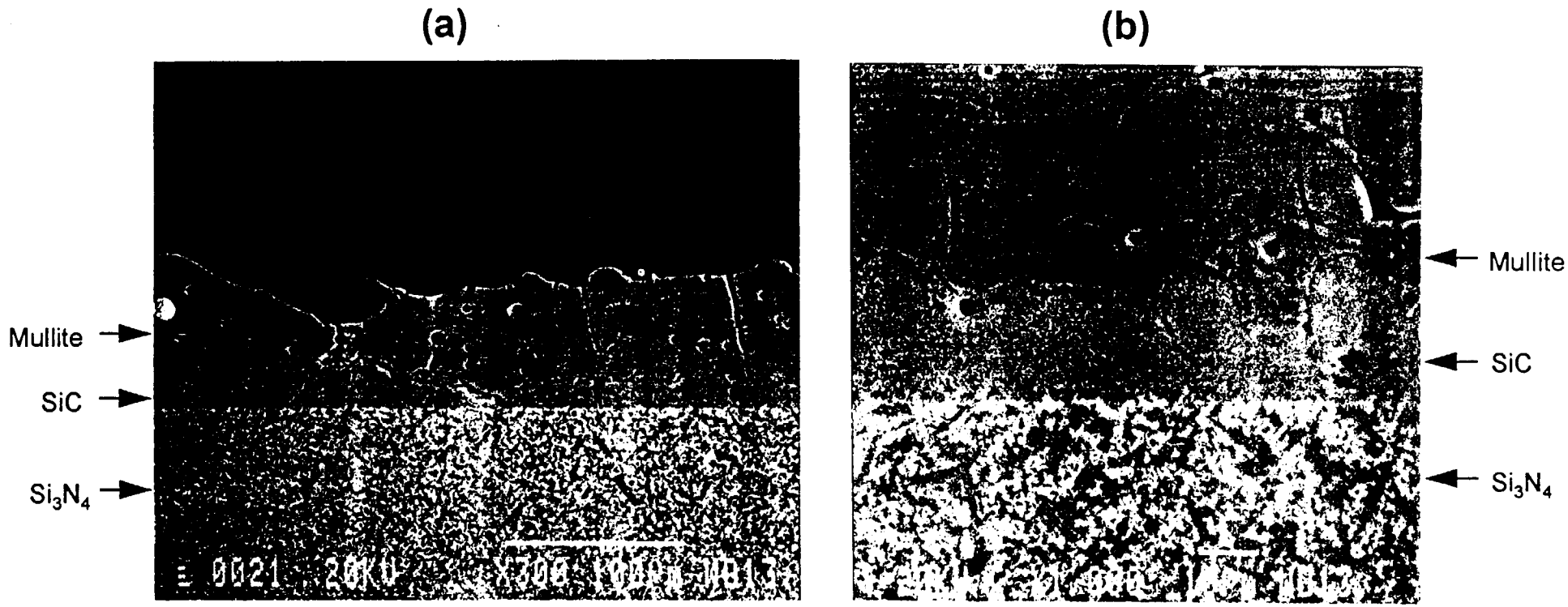

Fig. 1 CVD SiC/plasma-sprayed mullite dual layer coating on Si_3N_4 after 10 two-hour cycles between room temperature and 1200°C, exhibiting excellent adherence.

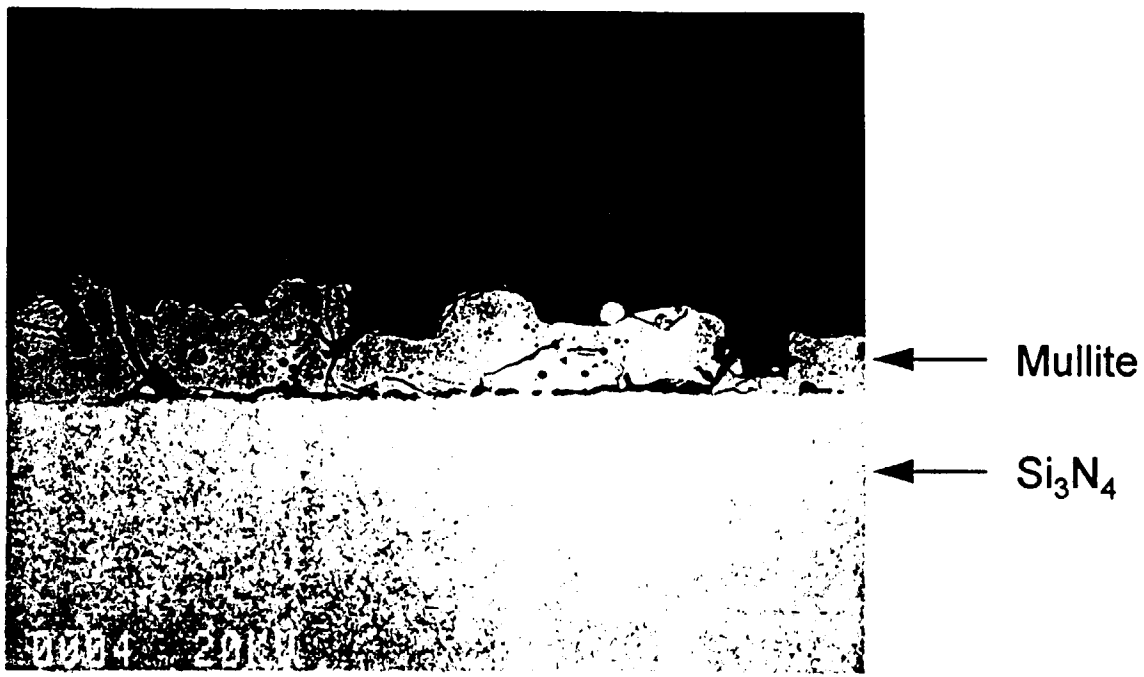

Fig. 2 Plasma-sprayed mullite coating on Si_3N_4 after 10 two-hour cycles between room temperature and 1200°C, exhibiting substantial debonding.

National Aeronautics and
Space Administration

Lewis Research Center
Cleveland, Ohio
44135

NASA

March 27, 1995

Reply to Attn of

Attn: Mr Charls Urbancic
Research Services
Cleveland State University
Cleveland, OH 44115

Dear Mr. Urbancic:

Enclosed is an invention disclosure entitled, "CVD SiC/Plasma-Sprayed Mullite Dual Layer Coating System for Silicon Nitride Ceramics".

I recommend that Cleveland State University assigns the right of the invention to NASA-Lewis Research Center based on the fact that this invention is of great interest to NASA-Lewis and NASA-Lewis has the facility and expertise to optimize the process, fabricate model parts, and perform critical tests, leading to the practical application.

Considering the technological implication of this invention and the need by NASA-Lewis, immediate attention on this matter will be greatly appreciated.

Sincerely,

Kang N. Lee